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Example 7

A Terpolymer of 15 Mole Percent DVS-bisBCB, 15 Mole Percent BCB Ethyl Acrylate and 70 Mole Percent BCB Acrylic Acid

DVS-bisBCB (9.59 g, 0.0246 mole), BCB ethyl acrylate (4.98 g, 0.0246 mole) and BCB acrylic acid (20 g, 0.115 mole) were heated in 105 g dipropyl glycol methyl ether acetate at 165° C. for 48 hours. The solution was cooled to room temperature. A film on the Si wafer was generated by spin-coating and curing at 250° C.

Example 8

Preparation of BCB-t-butyl Acrylate

A 5 liter three necked flask, equipped with a heating mantle, bottom dump valve, thermowell, reflux condenser and stirrer was charged with 1.43 grams of palladium acetate, 7.78 g of tris-(o-tolyl)-phosphine (TOTP), 356.8 g of 4-bromobenzocyclobutene (BrBCB), 250 grams of t-butyl acrylate, 385 g of potassium acetate, 585 mL of N,N-dimethylformamide (DMF) and 292 mL of deionized water. The reactor was degassed with a nitrogen sparge for 10 minutes and then heated to 93° C. After 19 hours a sample analyzed by capillary gas chromatography found no BrBCB and 91% trans-t-butyl acrylate BCB. After 22 hours the reactor was cooled and 1 liter of deionized water was added. The water layer was separated and discarded. The mixture was diluted with 1 liter of toluene and the organic phase washed with five 1-liter portions of deionized water. The organic phase was filtered through 150 mL of silica gel, topped with 40 g of magnesium sulfate on a membrane filter.

The toluene was removed by a rotary evaporator at aspirator vacuum using a 60° C. water bath, leaving 374.5 grams of crude product. The crude product was distilled at 120° C. and 0.005 torr. The overheads cut was 258.3 grams.

Example 9

Use of BCB-t-butyl Acrylate

BCB-t-butyl acrylate (34.5 grams), DVS-bisBCB (19.5 grams) and 162 grams of mesitylene were heated at 165° C. for over 66 hours. The solution was cooled to room temperature and filtered through a medium sintered glass filter. Part of the solution was spin-coated on a silicon wafer. The wafer was immersed in a TMAH solution. The spin-coated film started to break up in 10 seconds and dissolved in 50 seconds.

NMR spectra of DVS-bisBCB/t-butyl acrylate BCB prepolymers showed significant loss of the t-butyl group, ranging from 20% loss for a copolymer having 30 weight % t-butylacrylate BCB to 43% for a copolymer having 75 weight % t-butyl acrylate BCB. The presence of an acid group on the prepolymer was confirmed by IR spectroscopy. The IR spectra showed absorption at 1695 cm⁻¹ which is consistent with the presence of a carboxylic acid group.

Example 10

Use of DVS-bisBCB/BCB Acrylic Acid Copolymer in Wet Etching

DVS-bisBCB (17.60 grams, 0.0451 mol), BCB-acrylic acid (11.78 grams, 0.0677 mol) and mesitylene (28 grams) were heated with stirring under nitrogen at 165° C. for 69 hours. The solution was spread on a 4 inch wafer at 500 rpm followed by spin-coating at 3500 rpm. The wafer was baked on a hot plate at 100° C. for 2 minutes. A photoresist, Microposit 1400 from Shipley Company, was spread on top of the BCB film at 500 rpm for 1 second and spin-coated at 3000 rpm for 30 seconds. The wafer was baked in an oven at 100° C. for 15 minutes followed by exposure at 150 mJ/cm². The wafer was placed in a 2.3% Me₄NOH bath for

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10 minutes to remove photoresist and BCB film in exposed areas. Water was used to rinse the etched wafer. The etched wafer was dried and flood exposed at 200 mJ/cm². Photoresist was removed by putting the wafer in an Me₄NOH solution for 2 minutes. The wafer with a patterned BCB film was rinsed with water and cured.

Example 11

Use of DVS-bisBCB/BCB Acrylic Acid (mole ratio 30:70) in an Aqueous Base Developable Negative Tone Photoimaging System

DVS-bisBCB (28.0 grams, 0.072 mole), BCB acrylic acid (29.1 grams, 0.167 mole) and 172 grams mesitylene were heated at 160° C. for 174 hours. DVS-bisBCB to BCB acrylic acid was 30/70 and percentage of solids was 25. Some solvent escaped during B-staging and the solution concentration was 39% with viscosity at 128 Centipoise. Some mesitylene was removed to generate a solution with 49% solids.

The B-staged solution (1.76 grams, 0.862 g prepolymer) and 1,6-bis(4-azidobenzylidene)-4-ethylcyclohexanone (41.7 mg, 4.6%) were mixed. Cyclohexanone (0.12 grams) was added to generate a homogeneous solution. The solution was spin-coated on a 4 inch wafer at 1500 rpm. Prebake time at 95° C. was 110 seconds. The wafer was exposed at 300 mJ/cm² with a mask. Development was performed in a 1.4% TMAH solution for 2 minutes and 13 seconds. The wafer was baked at 75° C. for 1.5 hours and then cured. Patterned film thickness was 2.5 microns.

What is claimed is:

1. A curable polymer comprising the partially polymerized product of at least one cyclobutane monomer wherein the product comprises a pendant group comprising a —COOH moiety in amounts defined by equivalent weights in the range of about 200 to about 330 g/mole of —COOH moiety.

2. The polymer of claim 1 wherein the equivalent weight is in the range of about 220 to about 300 g/mole of acid functionality.

3. The polymer of claim 1 wherein the equivalent weight is in the range of about 230 to about 270 g/mole of acid functionality.

4. The polymer of claim 1 wherein the polymerization occurs in a solvent selected from di(propylene glycol) methyl ether acetate isomers; toluene; xylene; mesitylene; alcohols having from 3 to 6 carbon atoms; methylcyclohexanone; N-methylpyrrolidone; butyrolactone; and dipropylene glycol dimethyl ether isomers.

5. The polymer of claim 1 having a molecular weight in the range of 1000 to about 50,000 grams/mol.

6. The polymer of claim 1 having a molecular weight in the range of 1500 to 25,000 grams/mol.

7. The polymer of claim 1 having a molecular weight in the range of 2000 to 15,000 grams/mol.

8. A photoreactive polymeric composition comprising the polymer of claim 1 and a photoactive composition such that the polymeric composition is rendered either soluble or insoluble upon exposure to activating wavelengths of radiation.

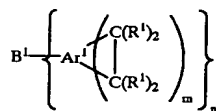
9. The polymeric composition of claim 8 wherein the photoactive composition comprises a dissolution inhibitor such that the polymeric composition is rendered soluble upon exposure to activating radiation.

10. The composition of claim 9 wherein the photoactive composition comprises a compound selected from sulfonylesters of trihydroxybenzophenone and cumyl phenol.

11. The composition of claim 8 wherein the photoactive composition comprises a photo-initiator that initiates further cure of the polymer upon exposure to activating radiation.

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12. The composition of claim 8 wherein the polymer or oligomer is the partially polymerized product of monomers comprising (a) a cyclobutarene monomer having the formula:



wherein

B¹ is an n-valent organic linking group,

Ar^1 is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar^1 ;

m is an integer of 1 or more;

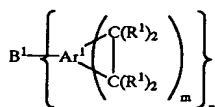
n is an integer of 1 or more; and

R^1 is a monovalent group; and

(b) is a cyclobutarene monomer comprising a —COOH moiety.

13. The polymer of claim 1, which is the partially polymerized product of monomers comprising:

(a) a cyclobutarene monomer having the formula:



wherein

B¹ is an n-valent organic linking group;

Ar¹ is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar¹:

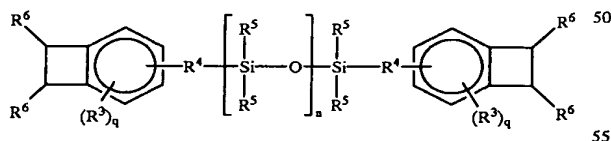
m is an integer of 1 or more;

n is an integer of 1 or more; and

R^1 is a monovalent group; and

(b) a cyclobutarene monomer comprising a —COOH moiety.

14. The polymer of claim 13 wherein monomer (a) has the following formula:

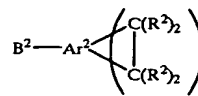


wherein each R³ is independently an alkyl group of 1-6 carbon atoms, trimethylsilyl, methoxy or chloro; each R⁴ is independently a divalent, ethylenically unsaturated organic group; each R⁵ is independently hydrogen, an alkyl group of 1 to 6 carbon atoms, cycloalkyl, aralkyl or phenyl; each R⁶ is independently hydrogen, an alkyl group of 1 to 6 carbon atoms, chloro or cyano; n is an integer of 1 or more; and each q is an integer of 0 to 3.

15. The polymer of claim 14 wherein R^4 is $-\text{CH}_2=\text{CH}_2-$, R^5 is methyl, R^6 is hydrogen, n is 1 and q is 0.

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16. The polymer of claim 13 wherein the monomer (b) has the following formula:



wherein

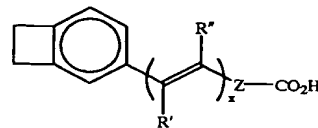
B² is a monovalent organic group comprising a —COOH moiety;

Ar^2 is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar^2 .

p is an integer of 1 or more; and

R^2 is a monovalent group.

17. The polymer of claim 13 wherein monomer (b) has the formula:



wherein

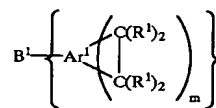
R' and R" are independently selected from hydrogen, alkyl groups of 1 to 6 carbon atoms, aryl groups, or R' and R" taken together from a cyclic group of 4 to 8 carbon atoms;

Z is a carbon-to-carbon bond or an aryl group; and

x is an integer from 0 to 3.

18. The polymer of claim 1, which is the partially polymerized product of monomers comprising:

(a) a cyclobutarene monomer having the formula:



wherein

B¹ is an n-valent organic linking group;

Ar¹ is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar¹;

m is an integer of 1 or more;

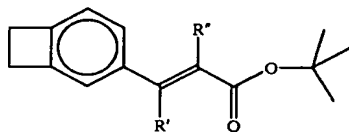
n is an integer of 1 or more; and

R^1 is a monovalent group; and

(b) is a cyclobutarene monomer having a pendant group, which at least partially converts to a carboxylic acid moiety during the polymerization process or by hydrolysis.

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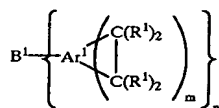
19. The polymer of claim 18 wherein (b') has the formula



wherein R' and R'' are independently selected from hydrogen, alkyl groups of 1 to 6 carbon atoms, aryl groups, or R' and R'' taken together from a cyclic group of 4 to 8 carbon atoms.

20. A process for making the polymer of claim 1 comprising the steps of

- (1) combining, in a solvent selected from di(propylene glycol) methyl ether acetate isomers; toluene; xylene; mesitylene; alcohols having from 3 to 6 carbon atoms; methylcyclohexanone; N-methylpyrrolidone; butyrolactone; and dipropylene glycol dimethyl ether isomers, a monomer (a) having the formula



wherein

B¹ is an n-valent organic linking group,

Ar¹ is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar¹;

m is an integer of 1 or more;

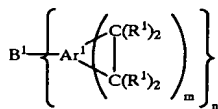
n is an integer of 1 or more;

with a monomer selected from monomer (b), which is a cyclobutene monomer comprising a carboxylic acid moiety and the monomer (b'), which is a cyclobutene monomer having a pendant group, which at least partially converts to a carboxylic acid moiety during the polymerization process; and

- (2) heating the combination to react with the monomers.

21. A partially polymerized product of monomers comprising

a cyclobutene monomer (a) having the formula:



wherein

B¹ is an n-valent organic linking group;

Ar¹ is a polyvalent aromatic or heteroaromatic group and the carbon atoms of the cyclobutane ring are bonded to adjacent carbon atoms on the same aromatic ring of Ar¹;

m is an integer of 1 or more;

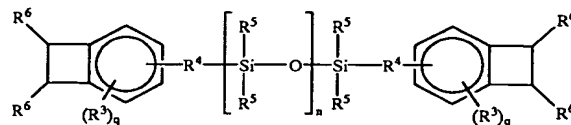
n is an integer of 1 or more; and

R¹ is a monovalent group; and

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(b') is a cyclobutene monomer having a pendant group, which at least partially converts to a carboxylic acid during the polymerization process.

22. A curable polymer comprising the partially polymerized product of (a) a monomer of the formula:



wherein

each R³ is independently an alkyl group of 1–6 carbon atoms, trimethylsilyl, methoxy or chloro;

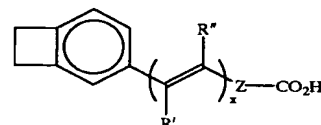
each R⁴ is independently a divalent, ethylenically unsaturated organic each R⁵ is independently hydrogen, an alkyl group of 1 to 6 carbon atoms, cycloalkyl, aralkyl or phenyl;

each R⁶ is independently hydrogen, an alkyl group of 1 to 6 carbon atoms, chloro or cyano;

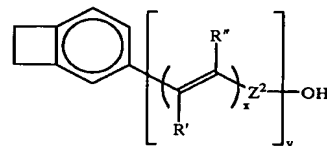
n is an integer of 1 or more; and

each q is an integer of 0 to 3; and

(b) is a monomer of one of the following formulas:

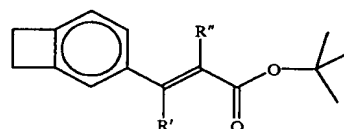


(i)



(ii)

and



(iii)

wherein

R' and R'' are independently selected from hydrogen, alkyl groups of 1 to 6 carbon atoms, aryl groups, or R' and R'' taken together from a cyclic group of 4 to 8 carbon atoms;

Z is a carbon-to-carbon bond or an aryl group;

x is an integer from 0 to 3;

y is 0 or 1; and

Z² is an aryl group.

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